



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : G02B 6/44, C03C 25/02, C08F 20/00	A1	(11) International Publication Number: WO 99/38043 (43) International Publication Date: 29 July 1999 (29.07.99)
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(21) International Application Number: PCT/NL99/00034

(22) International Filing Date: 19 January 1999 (19.01.99)

(30) Priority Data:
09/010,679 22 January 1998 (22.01.98) US

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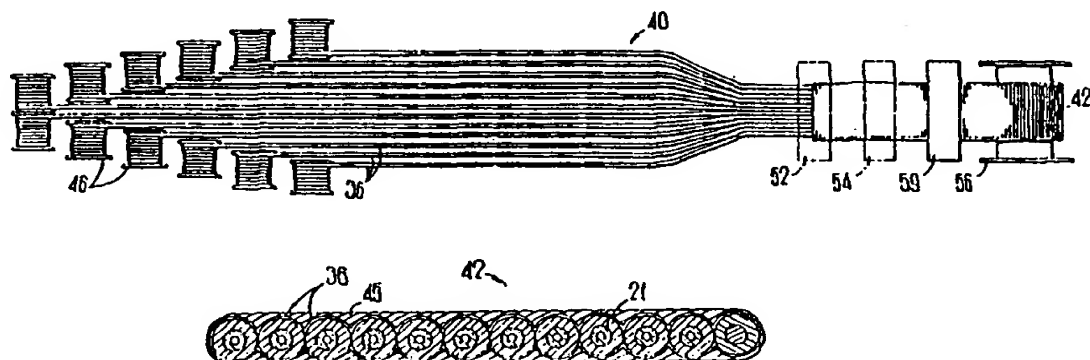
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(81) Designated States: AU, CA, JP, KR, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: RADIATION-CURABLE CROSS-LINKED RIBBON MATRIX OR BUNDLING MATERIAL FOR BONDING COATED OPTICAL GLASS FIBERS



(57) Abstract

A radiation-curable, cross-linked ribbon matrix material is suitable for covering an array of coated optical glass fibers. The matrix material contains at least one radiation-curable oligomer or monomer, and at least one chromophoric indicator selected so as to be susceptible to destruction of its chromophoric characteristic upon exposure to radiation and present in an amount which becomes substantially colorless when exposed to a level of radiation sufficient to cure the radiation-curable matrix material, wherein the at least one chromophoric indicator has a color that is distinguishable from a base color of the radiation-curable, optical glass fiber coating composition in cured form. A cable structure and a telecommunications system are also described.

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RADIATION-CURABLE CROSS-LINKED RIBBON MATRIX OR
BUNDLING MATERIAL FOR BONDING COATED OPTICAL GLASS
FIBERS

5 This invention relates to radiation-
curable, optical glass fiber ribbon matrix material for
bonding an array of optical glass fibers and to a
method of controlling the cure thereof.

10 BACKGROUND OF THE INVENTION

Optical glass fibers are generally coated
with two superposed radiation-cured coatings, which
together form a primary coating. The coating which is
in direct contact with the glass is called the inner
15 primary coating and the overlaying coating is called
the outer primary coating. A plurality of these coated
optical glass fibers may be assembled together and
bonded with matrix material to form a ribbon of
parallel coplanar coated optical fibers. Such a ribbon
20 may typically contain 12 coplanar optical fibers, but
other numbers of fibers like 2, 4 or 24, may be used to
form a ribbon. The fibers may also be bundled into a
circular or other shape of array forming a cylindrical
or other shape of structure having an outer coating of
25 ribbon matrix material. For example, a plurality of
ribbons can be assembled together to form bundles,
which bundles have bundling material to bond the
plurality of ribbons. The bundling material can be the
same as the matrix material.

30 The inner primary coating is usually a
relatively soft coating providing environmental
protection to the glass fiber and resistance, inter
alia, to the well-known phenomenon of microbending.
Microbending in the coated fiber can lead to
35 attenuation of the signal transmission capability of
the coated fiber and is therefore undesirable. The

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outer primary coating, which is on the exposed surface of the coated fiber, is typically a relatively harder coating designed to provide a desired resistance to physical handling forces, such as those encountered when the fiber is cabled.

Such primary coating systems are typically prepared from radiation-curable, optical glass fiber coating compositions (hereinafter referred to as "radiation-curable composition"). It is a characteristic of such systems that the curing proceeds upon exposure to a radiation source, typically a UV-radiation source, for a time sufficient to provide a full cure of the coating compositions at the level of intensity of such source.

As the demand for coated optical glass fibers has increased, manufacturers must respond by adding more fiber drawing production lines and by attempting to increase the linear line speeds of the existing fiber drawing production lines. In the latter case, one factor which will determine the upper limit for the line speed will be the curing rate characteristics of the radiation-curable compositions, including the ribbon matrix material, for a given radiation source and intensity.

If the line speed is increased to the extent that sufficient cure time for the radiation-curable composition, including the ribbon matrix or bundling material, is not provided, the radiation-curable composition will not have received a sufficient amount of radiation for complete cure, or cross-linking, of the radiation-curable composition. The production linear line speed is generally inversely related to the amount of radiation striking the optical glass fiber. That is, as the production line speed is increased the amount of radiation exposure to the radiation-curable composition during the production process will necessarily decrease for a given radiation

source. Incomplete cure of the radiation-curable composition is undesirable and must be avoided because then the desired protective properties of the incompletely cured primary coating may not be achieved and/or the incompletely cured primary coating may retain tackiness (giving problems in subsequent handling) or a malodorous odor may be present, and there may also be an increase in the extractables (undesirable) in the supposedly-cured coating.

10 Ribbon production, bundled ribbon production as well as fiber production is therefore confronted with the problem that increases in production line speed are difficult to achieve without jeopardizing the cured coating quality.

15 If the production line speed is increased without careful consideration and balancing of the associated reduction in radiation exposure, then the radiation-curable composition may be processed at a radiation exposure level less than required for the desired level of curing, which means that the cured primary coating or the ribbon matrix material may not be fully cured. However, if the line speed is conservatively adjusted downwards to ensure that an adequate cure is achieved, this means that the line production is correspondingly reduced at the expense of product throughput.

25 Because the amount of radiation exposure is equal to the radiation intensity multiplied by the exposure time, the desired or required production line speed could be achieved by increasing the radiation intensity. This would require larger radiation units, which could lead to problems and costs in designing and operating the production line. Even though adjustments in the radiation intensity or exposure can be made, there remain certain fundamental practical issues associated with a radiation curing lamp assembly which can affect the actual amount of radiation reaching a

radiation-curable composition, such as a ribbon matrix material.

Specifically, the amount of radiation striking the radiation-curable composition from, for instance, a UV-curing lamp system on a ribbon production line is not constant over the operative lifetime of the lamp and may be considered to be determined by the sum of the following:

- (1) reflectivity of lamp reflector system,
- (2) intensity of curing lamp output, and
- (3) surrounding enclosure of radiation-curable material.

The reflector system's ability to reflect the radiation can vary during production runs due to:

- (1a) variability of reflector cleanliness,
- (1b) misalignment of reflector system with radiation-curable composition,
- (1c) solarization of the reflector system,
- (1d) the age of the lamp and system itself.

The radiation curing UV lamp output typically changes in intensity as the bulb ages in use. Moreover, the wavelength distribution of lamp emission can change as a result of its aging during such use.

When curing radiation-curable compositions such as ribbon matrix material, an elliptical reflector system containing a UV curing lamp is usually used. Such a system is shown in Fig. 1.

As shown in Fig. 1, the UV lamp shown at 5 is positioned at one focal point of the elliptical reflector system shown at 3. A clear center tube shown at 7 is positioned around the other focal point of the reflector system shown at 3. The optical glass fiber or ribbon shown at 9, having a liquid radiation-curable composition thereon, passes through the center tube 7. The clear center tube 7 is also flushed with an inert atmosphere such as nitrogen or argon gas to reduce the oxygen inhibition of polymerization. The clear center

tube 7 also provides protection of the elliptical reflector system from contamination by the liquid coating as it is applied to the ribbon of optical fibers, e.g. by splattering.

5 During the radiation curing production process, the inner surface of the clear center tube 7 may, over time, become contaminated with some of ribbon matrix material or its components. This contamination has the effect of thereby decreasing the amount of
10 radiation which reaches the uncured coating on the ribbon array of optical glass fibers 9 after passage through the center tube 7.

 Thus, there is a need for some means to monitor and determine the level of cure of the ribbon
15 matrix material during the prolonged operation of the coating line. Since, once installed, the line apparatus and its radiation source are not readily changed except by expensive shut-down of the (generally continuously operating) line itself, the amount of radiation
20 actually striking the radiation-curable ribbon matrix material present on the array of optical glass fibers will necessarily vary, depending on the condition at any given point in time as a result of the above-described problems presented by the reflector system,
25 lamp output, contaminated center tubes.

 It is accordingly difficult to confidently meet the demand for increased production line speeds while maintaining conditions which will assuredly provide optimum complete cure of the coating. At the
30 present time, testing of the completeness of the ribbon matrix material cure is commonly done by off-line physical tests on specimens of the ribbon after it has been produced.

 What would be desirable is a system which
35 would permit real time determination of the ribbon matrix cure level by indicator means. Knowing whether or not the required complete cure is achieved under the

operating conditions will then inform the line operator of the need to make adjustments to line speed, lamp intensity (if possible) or replacement, or equipment cleaning, while not jeopardizing wasted production due to an inadequate coating cure.

There has been no effective solution to the above described problems for the glass fiber ribbon technology, until the present invention.

A process and apparatus for producing a bonded ribbon of coated fibers is described in U.S. Patent Nos. 5,037,763 and 4,900,126, the entire disclosures of which patents are incorporated herein by reference.

SUMMARY OF THE INVENTION

In view of the above described problems, an objective of the present invention is to provide a simple and effective real-time means to determine whether a radiation-curable ribbon matrix or bundling material applied to an array of optical glass fibers has been exposed to the required amount of radiation sufficient to reach the necessary level of cure.

The array may be a ribbon or a bundle of coated optical fibers. A typical ribbon may be formed from a row of 12 or 16 fibers. A typical bundle may be a substantially circular array having a central fiber surrounded by a plurality of further fibers. Alternatively, the bundle may have other appropriate cross-sectional shapes such as square, trapezoid, etc. The terms "ribbon" and "bundle" as used herein are interchangeable and non-limiting. The term "an array of coated optical fibers" as used herein means coated fibers or a plurality of coated and ribbonized optical fibers.

More particularly, this invention provides a technique whereby the optical glass fiber ribbon matrix material is provided with a chromophoric

component which has the property of losing its visible light chromophoric functionality upon exposure to UV actinic radiation and does so at a minimal concentration level such as to coincide with the level of radiation exposure which is required to achieve cure of the ribbon matrix material itself during the operation of the production line. This invention thus requires two balanced selection steps: first, the selection of the suitable chromophoric component, and secondly the selection of the concentration of that component in the ribbon matrix material. At the same time, the desired protective characteristics of the ribbon matrix material itself must not be degraded by addition of the chromophoric entity.

Surprisingly, this objective, and other objectives, are achieved by the following.

The invention provides a radiation-curable, cross-linkable optical glass fiber ribbon matrix material including at least one radiation-curable oligomer or monomer; and

at least one chromophoric indicator selected so as to be susceptible to destruction of its chromophoric characteristic upon exposure to actinic radiation and present in an amount which becomes substantially colorless when exposed to a level of radiation sufficient to cure said radiation-curable, optical glass fiber ribbon matrix material wherein said at least one chromophoric indicator has a color which is distinguishable from a base color of said radiation-curable, optical glass fiber ribbon matrix material in cured form.

The invention also provides a method of formulating a radiation-curable ribbon matrix material adapted for use on already coated optical glass fibers so as to provide a visual indication of a desired cure, said method comprising the steps of:

providing a radiation-curable, optical

glass fiber ribbon matrix material;

measuring and determining a critical radiation dose level for said radiation-curable, optical glass fiber ribbon matrix material which is the minimum level of radiation sufficient to achieve a desired cure of said radiation-curable, optical glass fiber ribbon matrix material;

selecting a chromophoric indicator having the characteristics of exhibiting a visible color while also having its chromophoric characteristics substantially destroyed upon exposure to actinic radiation;

determining a concentration of a chromophoric indicator that exhibits a substantially colorless characteristic at said critical radiation dose level for curing of said ribbon matrix material; and

incorporating at least said concentration of said chromophoric indicator into said uncured radiation-curable, optical glass fiber ribbon matrix material prior to application to a coated optical glass fiber.

The completeness of the cure of the matrix material can be determined by using an in-line colorimetric method to measure the chromophoric indicator.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates a schematic diagram of a conventional elliptical reflector system containing a UV curing lamp.

Fig. 2 illustrates a graph of an ultimate property of a ribbon matrix material versus the radiation dose applied to cure the ribbon matrix material.

Fig. 3 illustrates a graph of the equilibrium modulus of a radiation-cured ribbon matrix material versus the radiation dose applied to cure

the ribbon matrix material.

Fig. 4 illustrates a graph of the amount of discoloration of a specific concentration of a chromophoric indicator versus the radiation dose applied to the chromophoric indicator.

Fig. 5 illustrates a graph of the concentration of a chromophoric indicator versus the radiation dose required to completely bleach the chromophoric indicator.

Fig. 6 illustrates a schematic diagram of a production line for making an assembly of coated optical glass fibers formed into an array and coated with ribbon matrix material.

Fig. 7 illustrates, an end sectional view of a ribbon assembly of the invention.

Fig. 8 illustrates an end sectional view of another ribbon assembly of the invention.

Figs. 9-11 illustrate end sectional views of further ribbon assemblies of the invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Radiation-curable compositions usually exhibit the behavior shown in Fig. 2. As shown in Fig. 2, as the amount of radiation to which a radiation-curable composition is exposed is increased, the amount of a specific physical or performance property of the cured material (measured as a percentage of the fully attainable value for the specific composition) correspondingly increases. This increase continues until the ultimate value of the measured physical or performance property is achieved. The ultimate value is defined as the maximum value of a physical or performance property, which cannot be exceeded by further exposure to radiation. Examples of measured physical or performance properties are modulus, glass transition temperature, hardness, surface adhesion, and remaining extractables.

As shown in Fig. 2, once the measured physical property or performance property reaches the ultimate value, further exposure to radiation does not result in an increase in the measured property or performance. The lowest radiation dose which achieves the level of curing sufficient to provide the ultimate value is hereinafter referred to as the critical radiation dose " D_c ", and can be easily obtained from the graph in Fig. 2. D_c is used herein to represent minimum level of radiation exposure to fully cure the radiation-curable composition. By adjusting the radiation exposure in the fiber ribbon production line closely to the D_c , and being able to determine in real time that the D_c is just being maintained to effect the desired full cure, the linear line speed can be maximized without jeopardizing the product quality.

The following example demonstrates a simple way to determine the D_c required to achieve the ultimate value for the property of equilibrium modulus, according to this invention. Fig. 3 shows the graph of equilibrium modulus (MPas), (megapascals), versus the radiation dose (Joules/cm²).

The ultimate value for the equilibrium modulus of this example material is 0.6 MPas, at a critical radiation dose, D_c , of 0.75 Joules/cm². The D_c can be easily read from the graph in Fig. 3, as shown at 1. The requirement for a production engineer is to produce a fully cured ribbon of an array of optical glass fibers and hence to ensure that the radiation-curable ribbon matrix material is always exposed to a radiation dosage of at least the D_c , which here is 0.75 Joules/cm².

According to this invention, for determination of the level of adequate radiation cure of the radiation-curable ribbon matrix composition, i.e. that it has been exposed to at least the D_c level of radiation, a chromophoric indicator is incorporated

into that composition, the indicator having been selected so as to have the characteristic of substantially, and permanently, losing its chromophoric characteristic (at the concentration employed) upon exposure to that D_c radiation level, so as to become essentially colorless in visible light.

The use of such a chromophoric indicator according to the present invention is applicable to all radiation-curable, ribbon matrix material compositions.

Examples of suitable radiation-curable compositions which may be used variously include those which are disclosed in U.S. patent numbers 4,624,994; 4,682,851; 4,782,129; 4,794,133; 4,806,574; 4,849,462; 5,219,896; and 5,336,563, all of which are incorporated herein by reference.

Such radiation-curable compositions contain one or more radiation-curable oligomers or monomers having at least one functional group capable of polymerization when exposed to actinic radiation. Suitable radiation-curable oligomers or monomers are now well known and within the skill of the art.

Commonly, the radiation-curable functionality used is ethylenic unsaturation, which can be polymerized through radical polymerization or cationic polymerization. Specific examples of suitable ethylenic unsaturation are groups containing acrylate, methacrylate, styrene, vinyl ether, vinyl ester, N-substituted acrylamide, N-vinyl amide, maleate esters, and fumarate esters. Preferably, the ethylenic unsaturation is provided by a group containing acrylate, methacrylate, or styrene functionality.

Another type of functionality generally used is provided by, for example, epoxy groups, or thiol-ene or amine-ene systems. Epoxy groups can be polymerized through cationic polymerization, whereas the thiol-ene and amine-ene systems are usually polymerized through radical polymerization. The epoxy

groups can be, for example, homopolymerized. In the thiol-ene and amine-ene systems, for example, polymerization can occur between a group containing allylic unsaturation and a group containing a tertiary amine or thiol.

The radiation-curable compositions may also contain a reactive diluent which is used to adjust the viscosity. The reactive diluent can be a low viscosity monomer containing having at least one functional group capable of polymerization when exposed to actinic radiation. This functional group may be of the same nature as that used in the radiation-curable monomer or oligomer. Preferably, the functional group present in the reactive diluent is capable of copolymerizing with the radiation-curable functional group present on the radiation-curable monomer or oligomer.

For example, the reactive diluent can be a monomer or mixture of monomers having an acrylate or vinyl ether functionality and an C_4 - C_{20} alkyl or polyether moiety. Particular examples of such reactive diluents include: hexylacrylate, 2-ethylhexylacrylate, isobornylacrylate, decyl-acrylate, laurylacrylate, stearylacrylate, 2-ethoxyethoxy-ethylacrylate, laurylvinyether, 2-ethylhexylvinyl ether, N-vinyl formamide, isodecyl acrylate, isooctyl acrylate, N-vinyl-caprolactam, N-vinylpyrrolidone, and the like.

Another type of reactive diluent that can be used is a compound having an aromatic group. Particular examples of reactive diluents having an aromatic group include: ethyleneglycolphenylether-acrylate, polyethyleneglycolphenyletheracrylate, polypropyleneglycolphenylether-acrylate, and alkyl-substituted phenyl derivatives of the above monomers, such as polyethyleneglycolnonylphenyl-etheracrylate.

The reactive diluent can also comprise a diluent having two or more functional groups capable of

polymerization. Particular examples of such monomers include:

- C₂-C₁₈ hydrocarbon-dioldiacrylates,
- C₄-C₁₈ hydrocarbondivinylethers,
- 5 C₃-C₁₈ hydrocarbon triacrylates, and the polyether analogues thereof, and the like, such as
- 1,6-hexanedioldiacrylate, trimethylolpropanetri-
- acrylate, hexanedioldivinylether, triethylene-
- 10 glycoldiacrylate, pentaerythritol-triacrylate, ethoxylated bisphenol-A diacrylate, and tripropyleneglycol diacrylate.

- If the radiation-curable functional group of the radiation-curable monomer or oligomer is an
- 15 epoxy group, for example, one or more of the following compounds can be used as the reactive diluent:
- epoxy-cyclohexane, phenylepoxyethane,
- 1,2-epoxy-4-vinylcyclohexane, glycidylacrylate,
- 1,2-epoxy-4-epoxyethyl-cyclohexane, diglycidylether of
- 20 polyethylene-glycol, diglycidylether of bisphenol-A, and the like.

- If the radiation-curable functional group of the radiation-curable monomer or oligomer has an amine-ene or thiol-ene system, examples of reactive
- 25 diluents having allylic unsaturation that can be used include:

- diallylphthalate, triallyltri-mellitate,
- triallylcyanurate, triallylisocyanurate, and
- diallylisophthalate.
- 30 For amine-ene systems, amine functional diluents that can be used include, for example:
- the adduct of trimethylolpropane, isophorondiisocyanate and di(m)ethylethanolamine, the adduct of hexanediol, isophoron-diisocyanate and dipropylethanolamine, and
- 35 the adduct of trimethylol propane, tri-methylhexamethylenediisocyanate and di(m)ethylethanolamine.

Other additives which can be used in the ribbon matrix composition include, but are not limited to, photoinitiators, catalysts, lubricants, wetting agents, release agents, antioxidants and stabilizers.

5 The selection and use of such additives is within the skill of the art.

Generally, according to the present invention, a specific concentration of the chromophoric indicator is incorporated within the desired radiation-
10 curable ribbon matrix material composition. The chromophoric indicator is selected so as to display a color to the human eye prior to exposure to the radiation cure, e.g. a color having a wavelength in the range of about 400 to about 700 nm. During exposure to
15 radiation, the chromophoric indicator changes from colored to substantially colorless, hereinafter referred to as bleaching. The color of the chromophoric indicator must be distinguishable from any desired base color of the cured ribbon matrix material so that a
20 distinct color change can easily be seen prior to exposure of the radiation-curable ribbon matrix composition to the D_c level of radiation.

The concentration of the chromophoric indicator present within the radiation-curable
25 composition can be adjusted so that the bleaching of the chromophoric indicator occurs at a radiation level which is substantially equal to or greater than the critical radiation dose D_c for the radiation-curable composition. Thereby, the disappearance of the visible
30 color serves as an indicator or a complete cure of the radiation-curable composition. Preferably, the concentration of the chromophoric indicator present in the radiation-curable composition is adjusted so that the bleaching of the chromophoric indicator occurs at a
35 radiation level which is substantially equal to the critical radiation dose D_c for the radiation-curable composition.

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Based on the disclosure herein, one skilled in the art will easily be able to select and to determine the concentration of chromophoric indicator which becomes substantially colorless at the radiation level "D_c" required to fully cure the selected radiation-curable ribbon matrix composition.

For a specific chromophoric indicator at a specific concentration, the amount of bleaching of the chromophoric indicator can be represented by the response curve shown in Fig. 4. This response curve can be easily determined and measured by one skilled in the art by exposing a specific concentration of the chromophoric indicator to varying levels of radiation, measuring the amount of bleaching that has occurred, and then plotting the results. The amount of radiation required to completely bleach the specific concentration of chromophoric indicator can be easily read from the graph, as shown at 10.

Generally, an increase in the concentration of the chromophoric indicator will result in an increase in the amount of radiation required to bleach the chromophoric indicator. Different concentrations of the chromophoric indicator can then be tested in the same manner as above to determine the amounts of radiation required to completely bleach the different concentrations. The results can be plotted, as shown in Fig. 5 at number 12, to make a concentration/radiation dose curve. This concentration/radiation dose curve can be used to easily determine the approximate concentration of the chromophoric indicator that will become colorless at the selected radiation dose level. For example, if the critical radiation dose D_c of the radiation curable composition is .75 Joules/cm², the dose response curve can be used as shown by the dotted line to determine the concentration of chromophoric indicator that will become colorless at this radiation dose level, shown at 14 in Fig. 5. For this specific

example, that concentration of the chromophoric indicator is about 1.25 % by weight. The same type of radiation that will be used to cure the radiation-curable ribbon matrix material should be used to
5 determine the concentration/radiation dose curve.

The required amount of radiation to bleach the specific concentration of the chromophoric indicator in the radiation-curable composition may vary from the estimate provided by the
10 concentration/radiation dose curve due to effects from the components in the radiation-curable composition. Therefore, the final concentration of the chromophoric indicator should be experimentally fine-tuned by measuring the amount of radiation required to bleach
15 the chromophoric indicator in the desired radiation-curable composition and then increasing the concentration of the chromophoric indicator if the bleaching occurs at too low of a radiation dose or decreasing the concentration of the chromophoric
20 indicator if the bleaching occurs at too high of a radiation dose.

Suitable amounts of the chromophoric indicator have been found to be between about 0.05 and about 5 % by weight of the total radiation-curable
25 ribbon material composition. Preferably, the amount of chromophoric indicator is between about .1 and about 2 % by weight.

The chromophoric indicator can be any dye or pigment which bleaches or becomes colorless when
30 exposed to radiation, in particular the type of radiation used to cure the radiation-curable ribbon matrix composition. For example, the chromophoric indicator can be an organic dye which becomes colorless upon exposure to UV radiation.

35 Preferably, the chromophoric indicator is a polymeric dye. The term polymeric dye is used herein to represent those dyes having a polymeric (polyol)

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backbone into which at least one chromophoric molecular entity has been chemically incorporated. The polymeric dye preferably has molecular weight between about 1000 to about 2500, and more preferably about 1200 to about 2200.

Examples of suitable polymeric dyes are disclosed in U.S. patent No. 4,507,407, the complete disclosure of which is incorporated herein by reference.

Commercial examples of suitable polymeric dyes presently include:

Reactint Blue X3LV;
Reactint Blue X17AB;
Reactint Orange X38;
Reactint Red X64;
Reactint Violet X80LT; and
Reactint Yellow X15,
available from Milliken Chemicals.

An advantage of using a polymeric dye is that the backbone is capable to become entangled within, or reacted with, the (cross-linked) ribbon matrix material composition. This significantly reduces or eliminates the possibility that the chromophoric indicator would contribute to cured material volatiles.

The polymeric dye can be easily modified by incorporating into the polymeric backbone at least one functional group capable of polymerization exposed to radiation. The radiation-curable functional group can be any one of those described herein above. In this manner, the polymeric dye can be cross-linked with the radiation-curable oligomers and monomers present in the coating composition upon exposure to radiation.

Fig. 6 shows schematically, the production of a ribbon assembly 42 of an array of coated optical fibers 40. Bonded ribbon 42 includes a plurality of coated optical fibers 36 each having a core, a cladding, and one or more layers fed from fiber

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suppliers 46. A planar array of optical fibers 36 is embedded in radiation-curable matrix material by application of the matrix material in liquid form using applicator 52, for example, a coating die. The material is then directed past radiation curing apparatus 54, such as the apparatus shown in Fig. 1 herein, for curing the matrix material. The cured, bonded ribbon 42 then passes an in-line cure detection system 59 before being taken up on winding spool 56. In-line detection system 59 includes a color detection system for determining whether sufficient color shift of the chromophoric indicator has taken place, i.e., for determining colorimetrically whether cure of the matrix material is complete. This determination and corresponding in-line ability to monitor that cure is complete greatly reduces wastage of ribbon assemblies that include coated optical fibers. Details of methods for bonding optical fibers into a ribbon or other assembly are found in U.S. Patent Nos. 5,037,763 and 4,900,126, the disclosures of which are incorporated herein by reference.

The optical fiber ribbon may be visually inspected in-line at location 59, shown in Fig. 6, to determine whether the ribbon matrix material has been completely cured. A suitable wave-length sensitive colorimetric device may be used at this point. If the color of the cured ribbon matrix material containing the chromophoric indicator is the same as the base color (without chromophoric indicator) of a fully cured ribbon matrix material, then the ribbon matrix material has been exposed to sufficient actinic radiation to provide a complete cure.

Alternatively, the optical fiber ribbon may be visually inspected at winding spool 56, shown in Fig. 6, to determine whether the ribbon matrix material has been completely cured. If the color of the cured ribbon matrix material containing a chromophoric

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indicator is the same as the base color (without chromophoric indicator) of a fully cured ribbon matrix material, then the ribbon matrix material has been exposed to sufficient actinic radiation to provide a complete cure.

Figs. 7-11, in which like numerals represent like parts, illustrate various ribbon assemblies that can be formed using ribbon matrix material according to the invention. Ribbon assembly 42 shown in each of Figs. 7-11 is formed of an array of individual optical fibers 21 each surrounded by at least one coating 36, the array of optical fibers being joined together into a ribbon by ribbon matrix material 45. Fig. 7 shows a ribbon assembly. Fig. 8 shows edge bonding of the coated fibers forming the ribbon assembly. Figs. 9-11 show arrays of optical fibers respectively having substantially rectilinear, trapezoid and circular cross-sectional shapes.

The figures illustrate non-limiting examples of assemblies of bonded fibers. The ribbon matrix material may be of lesser thickness than the outer diameter of the coated glass fiber (Fig. 8), of substantially the same thickness, or of greater thickness than the outer diameter of the coated glass fiber (Fig. 7). Any of these configurations of the ribbon matrix material with respect to the coated optical glass fibers may be used with other arrays of fibers, such as those shown in Figs. 9-11.

The invention is not limited to the ribbon matrix material having a chromophoric indicator as already discussed. In the event it is desired to produce a color-coated ribbon matrix for the optical glass fibers, it will then be appropriate to employ a chromophoric indicator having the characteristic of exhibiting a color which will sufficiently modify the desired ribbon color so as to be readily detected by a shift in the tint or hue of the resulting combination

of chromophores under the condition that the chromophoric indicator has received insufficient radiation to induce sufficient shift in the tint or hue thereof.

5 If a wave-length sensitive device is used to determine whether the color indicator has been bleached (i.e., whether the ribbon matrix material has been completely cured), the device can be used to send a signal to the operator (manual or automated) of the
10 ribbon matrix production line. For example, the wave-length sensitive device can be connected to a controller for the radiation intensity such that when the color indicator is insufficiently bleached, the radiation intensity can be adjusted by the wave-length
15 sensitive device to provide the level of bleaching desired. Alternatively, by connecting the wave-length sensitive device to a controller for the line speed of the ribbon matrix production line, the wave-length sensitive device can signal an adjustment of the line
20 speed to the maximum speed which will still achieve a complete cure.

 The coated optical glass fibers made according to this invention can be used to make cable structures and for telecommunication systems. Such
25 telecommunication systems typically include cables containing optical glass fibers, transmitters, receivers, and switches. The cables containing ribbons or bundles of optical glass fibers are the fundamental connecting units of telecommunication systems.

30 The ribbons of, or bundles of (ribbonized) coated optical glass fibers made according to this invention can be adapted for enclosure within a cable structure. The cable structure can be buried under ground or water for long distance connections, such as
35 between cities. Alternatively, the ribbons or bundles of coated optical glass fibers can be adapted for use in local area networks, such as for connecting offices

in high rise buildings, residential subdivisions, and the like.

The present invention will be further described by the following non-limiting example.

5

Example I

1 wt% of Reactint X38 Orange (Milliken Chemicals) was added to the following composition:

40 wt% urethane acrylate oligomer;
10 55 wt% mono functional acrylate;
3 wt% photoinitiator; and
1 wt% additive (siloxane).

The critical dose of radiation D_c for the composition is 1.0 Joule/cm².

15 The mixture was exposed to 1.0 Joule/cm² of UV radiation. The orange color was not completely bleached at this radiation level. Therefore, the composition was then exposed to another 1.0 Joule/cm², which completely bleached the orange dye.

20

Example II

0.5 wt% of Reactint X38 Orange (Milliken Chemicals) was added to the following composition:

50 wt% urethane acrylate oligomer;
25 45 wt% monofunctional acrylate;
3.5 wt% photoinitiator; and
1 wt% additive (siloxane)

The critical dose of radiation D_c for the composition is 0.75 Joule/cm².

30 The mixture was exposed to 0.75 Joule/cm² of UV radiation. The orange color was completely bleached at this radiation level.

CLAIMS

1. A radiation-curable cross-linked ribbon matrix material for covering an array of coated optical glass fibers, comprising:
 - at least one radiation-curable oligomer or monomer;
 - at least one chromophoric indicator selected so as to be susceptible to destruction of its chromophoric characteristic upon exposure to radiation and present in an amount which becomes substantially colorless when exposed to a level of radiation sufficient to cure said radiation-curable matrix material;
 - wherein said at least one chromophoric indicator has a color that is distinguishable from a base color of said radiation-curable matrix material in cured form; and
 - wherein said chromophoric indicator comprises a polymeric dye having a backbone that is capable of becoming entangled within or reacted with said matrix material.
2. A ribbon matrix material according to claim 1, wherein said polymeric dye contains at least one radiation-curable functional group.
3. A ribbon matrix material according to any one of claims 1-2, wherein said polymeric dye has a molecular weight of between about 1000 and about 2500.
4. A ribbon matrix material according to claim 3, wherein said polymeric dye has a molecular weight of between about 1200 and about 2200.
5. A ribbon matrix material according to any one of claims 1-4, wherein said chromophoric indicator is present in an amount of between about 0.05 and about 5 wt.%, based on the total weight of the ribbon matrix material.

6. A ribbon matrix material according to claim 5,
wherein said chromophoric indicator is present in
an amount of between about .1 and about 2 wt.%,
based on the total weight of the ribbon matrix
material.
7. A ribbon assembly of an array of coated optical
glass fibers comprising:
an array of optical glass fibers; and
at least one radiation-cured cross-linked ribbon
matrix material containing a bleached
chromophoric indicator, according to any one of
claims 1-6.
8. A ribbon assembly according to claim 7 wherein
the ribbon assembly is edge-bonded.
9. A ribbon assembly according to claim 7 wherein
the ribbon assembly has a substantially circular
cross-section.
10. A ribbon assembly according to claim 7 wherein
the assembly has a substantially rectilinear
cross-section.
11. A ribbon assembly according to claim 7 wherein
the assembly has a substantially trapezoid cross-
section.
12. An optical glass fiber cable structure
comprising;
(1) at least one coated optical glass fiber;
and
(2) a sheath covering said at least one coated
optical glass fibers, said sheath comprising a
radiation-cured, cross-linked matrix material
containing a bleached chromophoric indicator,
according to any one of claims 1-6.
13. A telecommunications system comprising:
an array of coated optical glass fibers coated
with at least one radiation-cured, cross-linked
matrix material according to any one of claims
1-6.

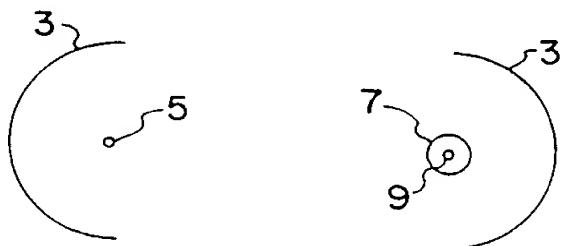


FIG. 1 (PRIOR ART)

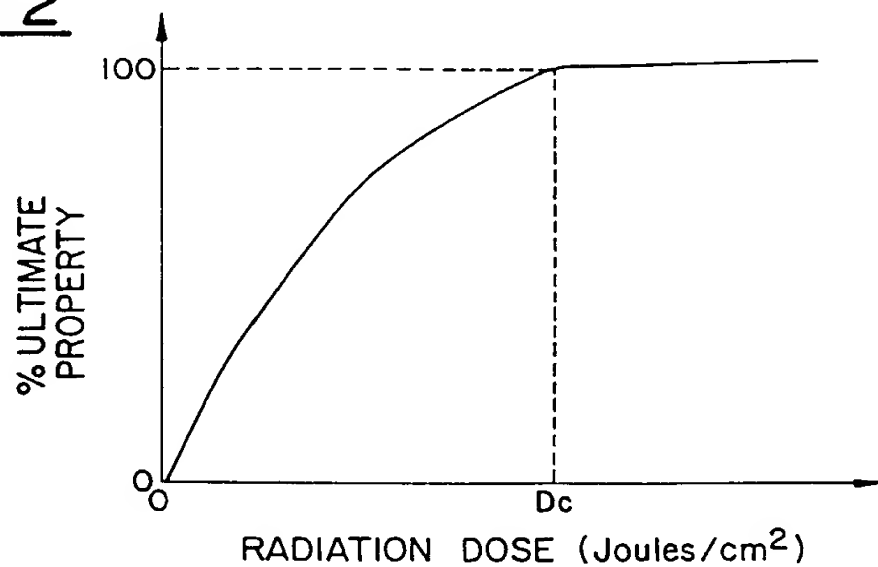
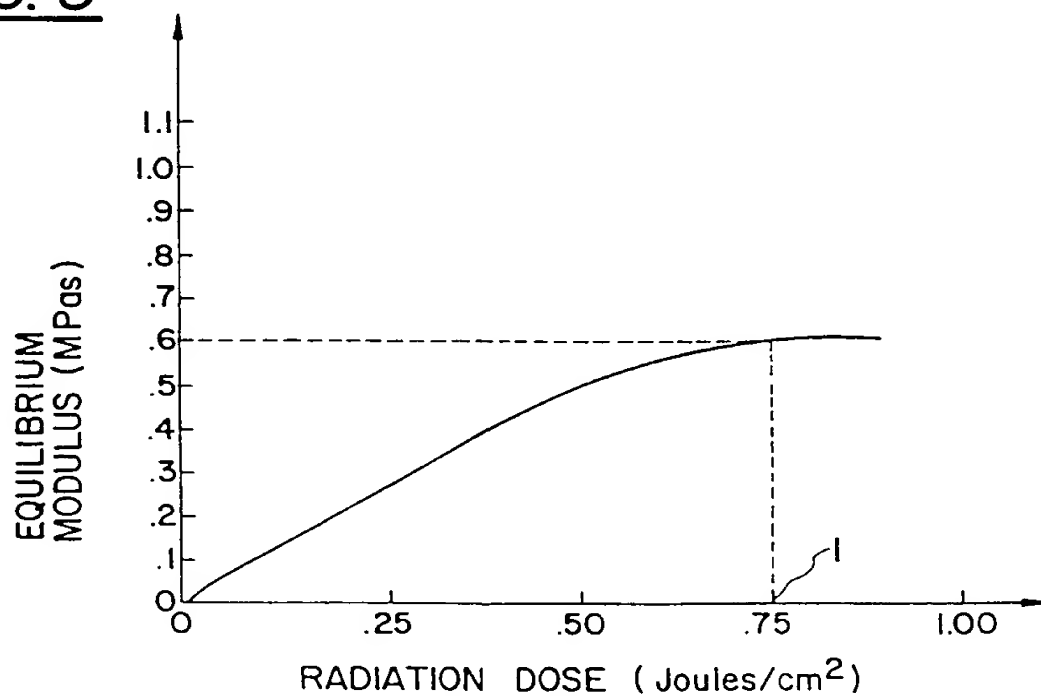
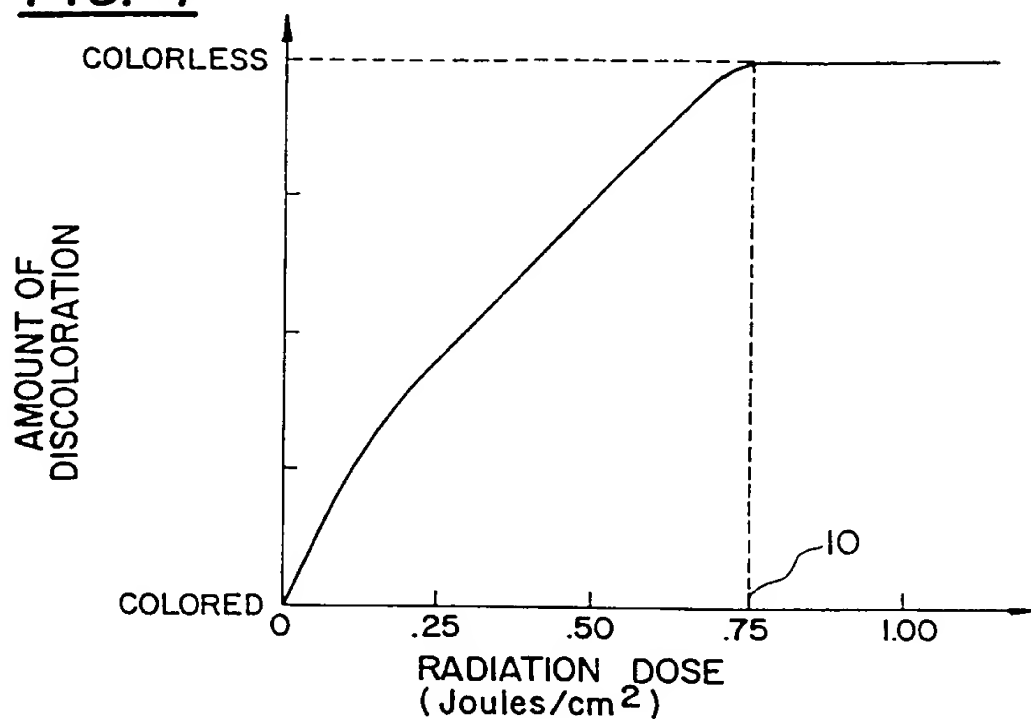
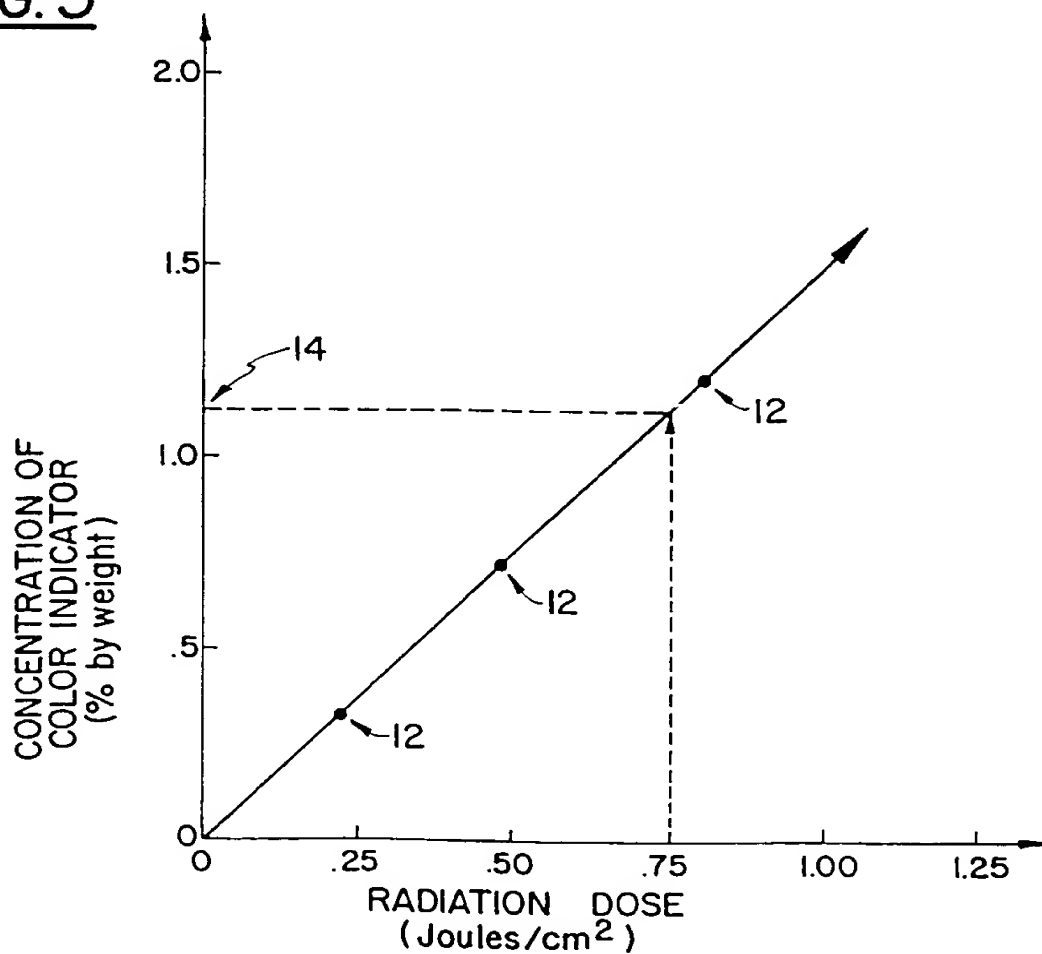
FIG. 2FIG. 3

FIG. 4**FIG. 5**

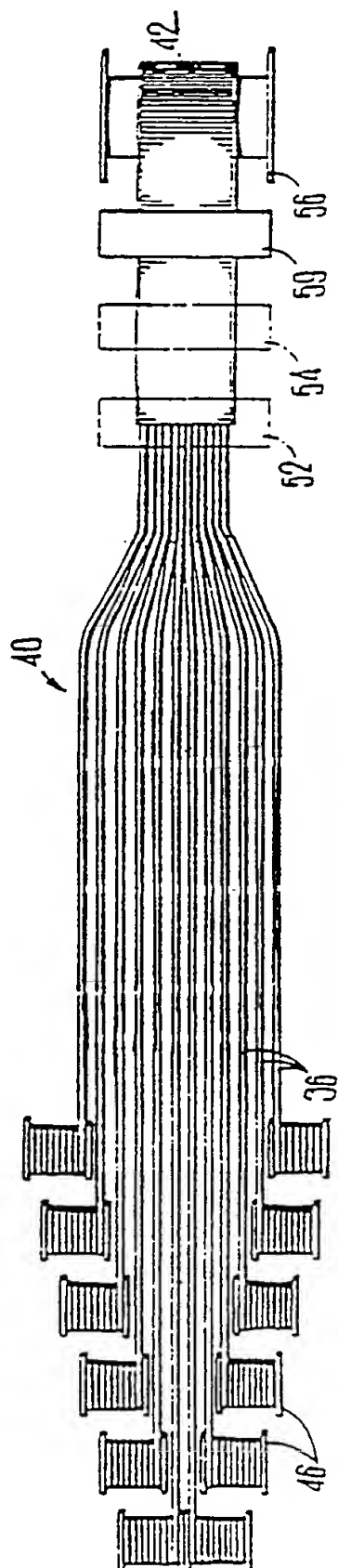


FIG. 6

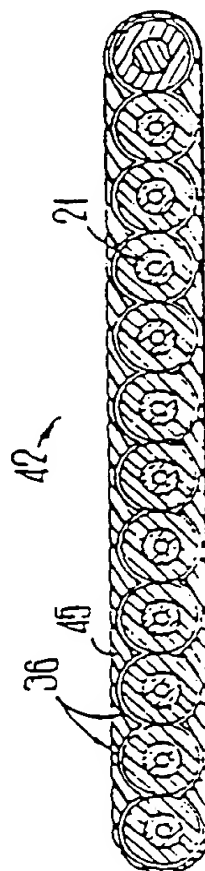


FIG. 7

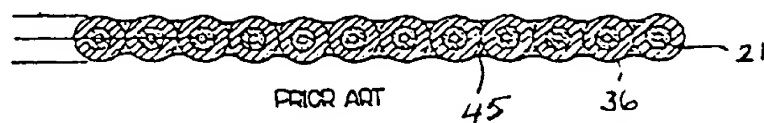


FIG. 8

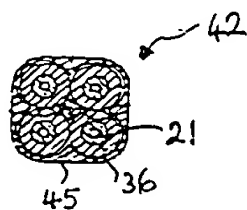


FIG. 9

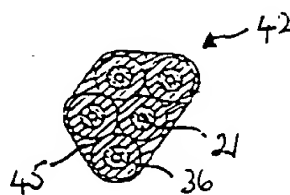


FIG. 10

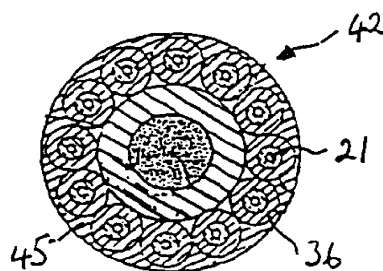


FIG. 11

INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/NL 99/00034

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G02B6/44 C03C25/02 C08F20/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G02B C03C C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 900 126 A (JACKSON KENNETH W ET AL) 13 February 1990 cited in the application see claims; figures ---	1,2,7-13
Y	PATENT ABSTRACTS OF JAPAN vol. 013, no. 510 (C-654), 15 November 1989 & JP 01 204902 A (DAINIPPON INK & CHEM INC), 17 August 1989 see abstract ---	1,2,7-13
Y,P	WO 98 03443 A (DSM NV) 29 January 1998 see claims; figures ---	1
Y	EP 0 390 415 A (AMERICAN TELEPHONE & TELEGRAPH) 3 October 1990 see claims; figures ---	1
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

18 March 1999

Date of mailing of the international search report

25/03/1999

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 99/00034

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 5 037 763 A (PETISCE JAMES R) 6 August 1991 cited in the application see claims; figures</p> <p>-----</p>	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Patent Application No

PCT/NL 99/00034

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4900126 A	13-02-1990	CA 1331530 A	23-08-1994
		CN 1039121 A,B	24-01-1990
		DK 323789 A	31-12-1989
		EP 0349206 A	03-01-1990
		JP 2047606 A	16-02-1990
		JP 2716212 B	18-02-1998
WO 9803443 A	29-01-1998	AU 3465997 A	10-02-1998
		US 5845034 A	01-12-1998
EP 0390415 A	03-10-1990	CA 2012263 A,C	30-09-1990
		JP 2651036 B	10-09-1997
		JP 3023240 A	31-01-1991
		US 5037763 A	06-08-1991
US 5037763 A	06-08-1991	CA 2012263 A,C	30-09-1990
		EP 0390415 A	03-10-1990
		JP 2651036 B	10-09-1997
		JP 3023240 A	31-01-1991

